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$Pb_4(BO_3)_2(SO_4)$ and $Pb_2[(BO_2)(OH)](SO_4)$: New lead(II) borate-sulfate mixed-anion compounds with two types of 3D network structures

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ABSTRACT

Two new lead(II) borate-sulfate mixed-anion compounds, namely, $Pb_4(BO_3)_2(SO_4)$ and $Pb_2[(BO_2)(OH)](SO_4)$, have been prepared by using high-temperature melt method or hydrothermal reaction. These compounds exhibit two different types of 3D structures composed of the same anionic units of BO_3 triangles and SO_4 tetrahedra which are interconnected by lead(II) cations. In $Pb_4(BO_3)_2(SO_4)$, the lead(II) ions are bridged by borate anions into 3D $[Pb_4(BO_3)_2]^{2+}$ architectures with 1D tunnels of 8-member rings along the *a*-axis, which are filled by the sulfate anions. In $Pb_2[(BO_2)(OH)](SO_4)$, the lead(II) ions are interconnected by borate and sulfate anions into 2D Pb-B-O and Pb-S-O layers parallel to the *ab* plane, respectively, and these layers are further condensed into the 3D lead(II) borate-sulfate framework. TGA and DSC studies indicate that $Pb_4(BO_3)_2(SO_4)$ is congruently melting with a melting point of 689 °C whereas $Pb_2[(BO_2)(OH)](SO_4)$ decomposes at approximately 335 °C. UV/Vis/NIR optical diffuse reflectance spectrum measurements reveal the optical band gaps of 4.03 and 4.08 eV for $Pb_4(BO_3)_2(SO_4)$ and $Pb_2[(BO_2)(OH)](SO_4)$, respectively. Furthermore, the electronic structures of $Pb_4(BO_3)_2(SO_4)$ have also been calculated.

1. Introduction

Borates and sulfates are two great types of compounds with rich structural diversities and various functional applications [1–18]. Recently, borosulfates, a new class of borate and sulfate derivative, have been developed through the combination of borate and sulfate anionic units in the same compounds, which raises the expectation for numerous new structural types [19–28]. It begins with $K_5[B(SO_4)_4]$, which was synthesized and structurally characterized in 2012 [19]. $K_5[B(SO_4)_4]$ features the unprecedented $[B(SO_4)_4]^{5-}$ anion. Subsequently, a series of borosulfates emerged. Within these structures of reported metal borosulfates, the boron atoms exhibit a strong tendency to adopt the BO_4 tetrahedral coordination geometry, rather than the trigonal-planar BO_3 mode. The basic units BO_4 and SO_4 condensed directly into various B-S-O anionic structures, such as isolated $[B(SO_4)_4]^{5-}$ in $A_5[B(SO_4)_4]$ (A = Li, Na, K, Rb) [19,22–24], $[B(S_2O_7)_2]^-$ in $A[B(S_2O_7)_2]$ (A = NH_4, Li, Na, K) [17,20,21], $[B_2O(SO_4)_4]^{4-}$ in $Rb_4[B_2O(SO_4)_4]$ [25] and $[B_2(SO_4)_6]^{6-}$ anions in $Gd_2[B_2S_6O_{24}]$ [21], one-dimensional (1D) $[B(SO_4)_2]^-$, $[B(SO_3)_3]^{3-}$, $[B(S_2O_7)(SO_4)]^-$ and $[B_2O(SO_4)_3]^{2-}$ chains in $Ag[B(SO_4)_2]$ [27], $A_3[B(SO_4)_3]$ (A = K, Rb) [24], $A[B(S_2O_7)(SO_4)]$ (A = H, Cs) [20] and $Ba[B_2S_3O_{13}]$ [21], two-dimensional (2D) $[B_2O(SO_4)_3]^{2-}$ layers in $Cs_2B_2S_3O_{13}$ [25] and $Ca_2B_2S_4O_{16}$ [28], respectively, and three-dimensional (3D) $[B(SO_4)_2]^-$ anionic network in $A[B(SO_4)_2]$ (A = H_3O, NH_4, Li, Na, K) [20,23,24]. It is notable that borosulfates exhibit rich interesting structural chemistry. However, due to the high formal charge of sulfur, there should be less possibility to achieve the direct condensation of SO_4 and BO_3 units, hence only tetrahedral BO_4 groups observed in the borosulfates reported.

Borate-sulfates is one other derivative of borate and sulfate which containing both B-O and S-O groups. Different from borosulfates, the B-O and S-O groups remain isolated with each other in the borate-sulfates and no B-O-S linkage is formed. Borate-sulfates have been studied for more than half a century, but have been ignored by scientists. Except for a series of rare earth borate-sulfates reported by our group very recently [29], only seven borate-sulfates, namely, $Pb_6O_2(BO_3)_2(SO_4)$, $Ca_3Na_2(B_5O_8)(SO_4)_2(OH)_2Cl$, $A_3H(SO_4)_2(B_2O_3)_2$ (A = Rb, Cs), $Mg_3(OH)_2(SO_4)(B(OH)_4)_2$, $Mg_3(B(OH)_4)_2(SO_4)(OH)F$, and $Ca_6Al_2(SO_4)_2(B(OH)_4)(OH,O)_{12}(H_2O)_{26}$ have been structurally characterized [25,30–34]. Compared to borosulfates, due to the isolated character between borate and sulfate anions, borate-sulfates exhibit more flexible coordination geometries and condensation modes

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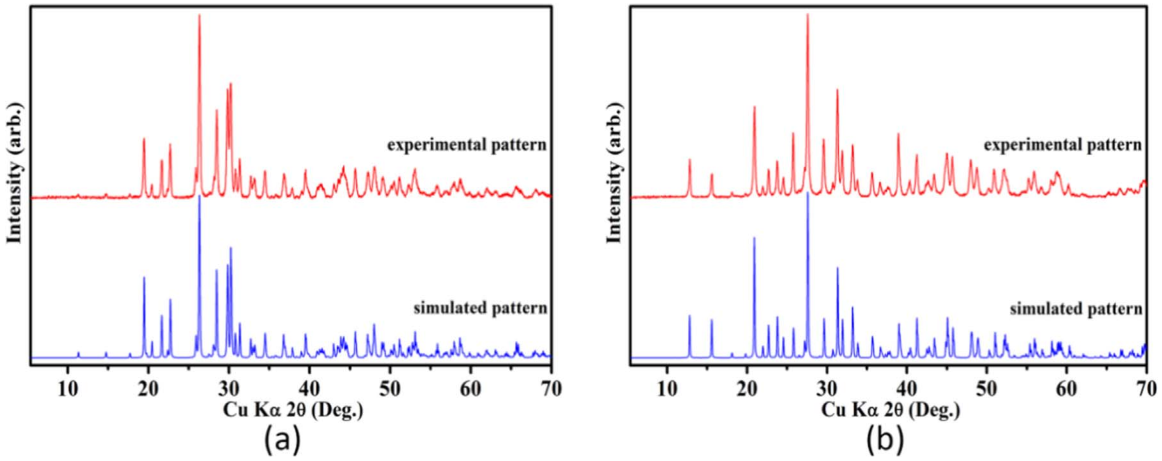

Fig. 1. Experimental and simulated powder X-ray diffraction patterns of $Pb_4(BO_3)_2(SO_4)$ (a) and $Pb_2[(BO_2)(OH)](SO_4)$ (b).

for borate anions. Both trigonal-planar BO_3 and tetrahedral BO_4 building units present in the structures of borate-sulfates. The BO_3 groups were condensed into a planar neutral $[B_2O_3]$ layer in $A_3H(SO_4)_2(B_2O_3)_2$ (A = Rb, Cs) [25], and the $[B_5O_8]^{3-}$ anionic cluster was formed by the condensation of BO_3 and BO_4 groups in $Na_2Ca_3(B_5O_8)(SO_4)_2(OH)_2Cl$ [31]. As we known, BO_3 unit is a promising anionic group with large microscopic second-order nonlinear optical (NLO) susceptibility [35]. Hence, exploring new borate-sulfates will result in rich structural chemistry and offer new opportunities for designing new NLO materials, which inspiring our research motivation in the metal borate-sulfates system.

To explore new borate-sulfates containing trigonal-planar BO_3 anionic units and further enrich the structural chemistry of metal borate-sulfates, we focused on the Pb-B-S-O systems. As we know, the Pb(II) cation contains a 6 s^2 lone pair electrons and usually exhibits a variety of asymmetric coordination geometries, which plays a role as a structural guide to improve the probability of the formation of asymmetric BO_3 anionic units in the crystal structures of lead(II) borates or borate derivatives [36–42]. The only reported Pb-containing borate-sulfates, namely $Pb_6O_2(BO_3)_2(SO_4)$, possesses the only BO_3 anionic units [30]. Due to the flexible coordination geometries of lead(II) cations and a variety of polynuclear lead(II) clusters can be formed, it is expected that other new lead(II) sulfates with BO_3 groups can be isolated under suitable conditions. In this work, two novel lead(II) borate-sulfates, namely, $Pb_4(BO_3)_2(SO_4)$ and $Pb_2[(BO_2)(OH)](SO_4)$, have been synthesized using the high-temperature melt method and hydrothermal method, respectively. Herein we report their syntheses, crystal structures, optical and thermal properties as well as electronic structures.

2. Experimental

2.1. Reagents and instruments

PbO (≥ 99.0%), $Pb(BO_2)_2\cdot H_2O$ (≥ 99.0%), $(NH_4)_2SO_4$ (≥ 99.0%) and H_3BO_3 (≥ 99.8%) were all purchased from Aladdin Reagent (Shanghai) Co., Ltd, while H_2SO_4 (95–98%) and $NH_3\cdot H_2O$ (25–28%) were both obtained from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received.

X-ray diffraction (XRD) patterns of powder samples were collected on a Rigaku MiniFlex II diffractometer using monochromated Cu-Kα radiation (λ = 1.540598 Å) with a step size of 0.02°. Microprobe elemental analyses were performed on a field emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy dispersive X-ray spectroscope (EDS, Oxford INCA). IR spectra were recorded on a Magna 750 FT-IR spectrometer as KBr pellets in the range of 4000–400 cm^{-1}. A PE Lambda 900 UV–vis spectrophotometer was used to record the optical diffuse reflectance spectra at room temperature. The UV–Vis–NIR optical diffuse reflectance spectra were measured at room temperature with a Perkin Elmer Lambda 950 UV–Vis–NIR spectrophotometer. A $BaSO_4$ plate was used as a standard (100% reflectance). The absorption (α/S) data were calculated from the reflectance spectra by using the Kubelka-Munk function $F(R) = (1-R)^2/2R = \alpha/S$, where α is the absorption coefficient, R is the reflectance, and S is the scattering coefficient which is practically wavelength independent when the particle size is larger than 5 μm [43]. The band gaps were estimated according to the intercept by extrapolating the straightest line to the $h\nu$ axis in the α/S vs $h\nu$ plot. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were carried out simultaneously on a NETZSCH STA449C instrument at a heating rate of 5 °C min^{-1} under a nitrogen atmosphere. For $Pb_4(BO_3)_2(SO_4)$, a heating process from room temperature to 720 °C, followed by an immediate cooling process from 720 °C to 200 °C, was used, while for $Pb_2[(BO_2)(OH)](SO_4)$, only a heating process from room temperature to 600 °C was included.

2.2. Syntheses

Polycrystalline samples of $Pb_4(BO_3)_2(SO_4)$ were synthesized by the solid-state reaction of the stoichiometric mixture of PbO (8 mmol, 1786 mg), H_3BO_3 (4 mmol, 247 mg) and $(NH_4)_2SO_4$ (2 mmol, 264 mg). The initial mixture was ground thoroughly in an agate mortar and then heated at 620 °C for 3 days with several intermittent grindings. The powder XRD pattern of the product agrees well with the simulated one, which confirms the purities of synthesized polycrystalline samples (Fig. 1a).

Crystals of $Pb_4(BO_3)_2(SO_4)$ were obtained through the high-temperature melt method. Polycrystalline samples of $Pb_4(BO_3)_2(SO_4)$ placed in a platinum crucible were heated at 700 °C for 2 h in muffle furnace, forming homogeneous transparent melt, and then cooled down to 550 °C at a rate of 3 °C h^{-1}, followed by cooling to room temperature at a rate of 20 °C h^{-1}。 Finally, transparent $Pb_4(BO_3)_2(SO_4)$ crystals were obtained. The energy-dispersive spectrometry (EDS) on several single crystals confirmed the presence of Pb, S, and B elements, and the average atomic ratio of Pb: S was determined to be 4.3:1.0, which matches well with the molecular formula determined from single-crystal X-ray structure analysis (Fig. S1a, ESI†).

$Pb_2[(BO_2)(OH)](SO_4)$ crystals were synthesized by hydrothermal reaction. Typically, $Pb(BO_2)_2\cdot H_2O$ (1 mmol, 310.8 mg), H_2SO_4 solution (0.1 mL), $NH_3\cdot H_2O$ (0.25 mL) and H_2O (3 mL) were sealed in a 23 mL Teflon-lined stainless-steel autoclave, and the pH value of the reaction mother liquid was about 5. The autoclave was heated at 220 °C for three days, and then cooled to room temperature at a rate of 3 °C h^{-1}. The reaction products were washed with water and then dried in air.